

## PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :		A1	(11) International Publication Number: WO 96/28517
C09C 3/06, 1/00, D21H 17/67, 19/38			(43) International Publication Date: 19 September 1996 (19.09.96)
(21) International Application Number: PCT/US96/03547		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 14 March 1996 (14.03.96)		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: 08/404,680 15 March 1995 (15.03.95) US			
(71) Applicant: MINERALS TECHNOLOGIES INC. (US/US); 405 Lexington Avenue, New York, NY 10174-1901 (US).			
(72) Inventors: SOHARA, Joseph, Andrew, 3346 Delong Avenue, Bethlehem, PA 18017 (US). YOUNG, Trudy, Diane, 255 Fleetow Road, Nazareth, PA 18064 (US).			
(74) Agents: RICHARDS, John; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.			
(54) Title: RECYCLING OF MINERAL FILLERS FROM THE RESIDUE OF A PAPER DEINKING PLANT			
<pre>     graph TD       DIR[DIR] -- "Heat 800°-1200°" --&gt; Ash[Ash + H2O + CO2 + Heat]       Ash --&gt; Slurry[Ca(OH)2/Ash Slurry]       CO2[CO2] --&gt; Slurry       Slurry --&gt; PCC[CaCO3 + H2O]   </pre>			
(57) Abstract			
<p>A method of recycling mineral pigments contained in the waste produced from the deinking of wastepaper. The deink residue is heated in an oxygen-containing atmosphere to a temperature sufficient to completely oxidize all the organic hydrocarbons present. Heat, water, and carbon dioxide also are generated and may be captured and reused in the process. Combustion causes a chemical reaction to occur, so that the original pigments contained in the deink residue are converted to new, stable mineral forms. The ash from the combustion is primarily a mixture of gehlenite (<math>Ca_2Al_2SiO_7</math>), anorthite (<math>CaAl_2Si_2O_8</math>) and perovskite (<math>CaTiO_3</math>). The ash containing the mixed mineral phases is added to a reactor in which carbon dioxide gas is bubbled through an aqueous slurry of calcium hydroxide so that precipitated calcium carbonate (PCC) is produced. Because the mineral phases in the ash contain calcium as part of their crystal structure, the PCC will precipitate and grow on the ash particles. This results in a "recycled" PCC pigment containing an ash "core". The properties of the recycled PCC are similar to virgin PCC.</p>			

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PA	Palestine
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	L1	Liechtenstein	SI	Slovenia
CI	Coat d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroun	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Lvavia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

RECYCLING OF MINERAL FILLERS FROM THE RESIDUE OF A  
PAPER DEINKING PLANT

Technical Field

This invention relates to the processing and  
5 reuse of mineral pigment fillers that are removed from  
paper as part of the deinking process. Such fillers  
are generally part of a complex mixture of wastes  
comprising mixed pigments (clays, calcium carbonates,  
titania, etc.), water, cellulose fibers, inks, toners,  
10 adhesives, etc. Generally, these wastes are either  
burned for the fuel content of the organic components  
or buried in a landfill. This invention describes a  
process for rendering these mineral fillers suitable  
for use as raw materials and as a substrate in a  
15 process to produce precipitated calcium carbonate (PCC)  
by the reaction of milk of lime ( $\text{Ca}(\text{OH})_2$ ) with carbon  
dioxide gas ( $\text{CO}_2$ ).

Background Art

The recycling of wastepaper generally  
20 involves separation of a usable pulp fiber from the  
other components of the paper, such as mineral fillers,  
printing inks, laser toner particles, and adhesives,  
through a series of steps that may be carried out in  
any way that is suitable to the purpose of the deinking  
25 plant and its customers. Regardless of the specific  
recycling process, two materials are always produced:  
(1) pulp fiber, called "secondary" fiber, that can be  
sold to a paper manufacturer for reuse as a raw  
material in the production of paper and (2) a composite

- 2 -

waste material comprising a mixture of components that are removed as part of the deinking process. The composite waste material is called deink residue (DIR).

5 The amount of DIR that is generated will vary depending on the quality of the incoming wastepaper and the type of recycling process. Typically, on a dry basis, the fraction of DIR will be 15 to 40 percent by weight of the original wastepaper before deinking. Since the DIR is produced in a wet state, before the 10 waste leaves the deinking process as much water as possible is removed to reduce handling and transportation costs. Generally, the waste is pressed to about 50 percent solids. Therefore, for every 100 tons of wastepaper processed, between 30 and 80 tons of 15 wet DIR, half of which is water, will be produced. By the end of 1996, deinking plants in North America will recycle upwards of 3.5 million tons of wastepaper, and, therefore, will generate upwards of 1 million tons of wet residue.

20 In deinking plants that operate on the site of a papermill and are integrated with the mill, the DIR is often burned for its fuel content in the mill's white liquor recovery boilers. However, because of its high water content, DIR is a low-grade, inefficient 25 fuel. In non-integrated deinking plants, the most common fate of the residue is a landfill. Landfilling is undesirable because it is both expensive and environmentally unfriendly. Thus, there has been a need to reduce the volume of waste generated at a 30 deinking plant by reusing the mineral fillers and/or other components present in the residue mixture.

35 Many grades of paper contain functional mineral pigments, such as kaolin clays, calcium carbonate, titania, silicates, etc., which are incorporated into the paper when it is made. There has been no practical method of separating the mineral pigments from the organic portion of the waste, so that

- 3 -

the mineral pigments can be reused in a product or process for making paper.

Previously, the wastes from papermaking or from recycling wastepaper have been incinerated, and 5 the residue of the incineration has been deposited in a landfill or used to produce aggregate materials, typically for use in construction applications. This residual ash typically makes up about 15-20 percent by weight of the original weight of DIR.

10 In U.S. Patent No. 4,932,336, a wet dewatered collected product of solids consisting predominately of cellulosic material (wood and cellulose fibers) and a residue consisting predominately of plastic pieces separated from waste paper prior to recycling are 15 recovered separately. The collected product is dried to a residual water content of no more than 25 percent by weight of the product, and continuously layered to form a continuously advancing layer. A layer of the residue is deposited on the product layer to form a 20 continuously advancing two layer bed, which is burned while bottom blowing the two layer bed with a gas containing air. In this process, the product and residue are destroyed, a combustion gas is produced, and a slag is recovered. Fly ash produced in the 25 process can be added to the slag to prevent its release into the environment, and the slag is either deposited in a landfill, or used in a structural material. The heat from the combustion gas can also be used as a heat source, especially for steam generation.

30 U.S. Patent No. 5,018,459 discloses a method and apparatus for the recycling of paper pulp sludge produced as a waste material in the manufacture of paper, cardboard, and related materials. The paper pulp sludge is continuously fed into a rotary kiln at a 35 temperature of between 800° and 3500°F. If the temperature is maintained above 2400°F, hazardous materials such as dioxins, formed in the incineration

- 4 -

process, are destroyed. Mixing catalysts, typically casein or soy protein, and wood pulp fibers are burned with the paper pulp sludge. The resulting incinerated product, consisting essentially of carbonate particles, 5 can be used as a mineral filler binding agent in the manufacture of asphalt, asphalt coatings and sealants, ceramics, concrete, cement pipe, clay pipe, structural block, and brick, or as an absorbent for spilled oil. In U.S. Patent No. 5,054,406, 15 to 25 percent by 10 weight of the product of the incineration of paper pulp sludge is mixed with earthen clay to form a water retardant material that is used to cover and seal landfills.

U.S. Patent No. 4,769,149 discloses a method 15 for the recovery of energy from waste and residues comprising bacterial digestion of the waste followed by incineration, wherein the methane gas produced during the bacterial digestion is used to heat the furnace. The heat released in the combustion process can then 20 used in an industrial process where it is required.

European Patent Application No. 0 604 095 discloses a process for treating a dilute aqueous 25 suspension of particulate waste material, such as the material found in paper mill effluent. Kaolin clays are exemplified as typical waste materials. The process comprises precipitating an alkaline earth metal carbonate, e.g., calcium carbonate, in the aqueous suspension of particulate material, such that the particulate material present at the start of the 30 process becomes entrained in the alkaline earth metal carbonate precipitate. Figure 1 of EPA 0604 095 shows a scanning electron micrograph of flat "platy" kaolinite particles entrained in aggregations of precipitated calcium carbonate particles. The 35 resulting agglomeration of calcium carbonate and entrained clay particles can be used as a paper filler or pigment.

- 5 -

There is still a need, however, for recycling of DIR in a manner that results in useful products rather than as landfill material. The present invention provides one such solution to this problem.

5

Summary of the Invention

The present invention provides a process for the recovery and reuse of mineral pigments from the residue produced when wastepaper is deinked and processed into secondary pulp fiber. This process 10 comprises heating the residue in an oxygen-containing atmosphere to a temperature, sufficiently high to completely oxidize all of the hydrocarbon materials in the deink residue to yield heat, carbon dioxide, and water, in addition to an ash formed from the non-combustible mineral pigments present in the wastepaper. 15 In the present invention, the mineral ash from the combustion is mixed with calcium oxide and water to form a slurry of calcium hydroxide and ash. A gas containing carbon dioxide, which may be filtered and 20 cooled flue gas, is bubbled into the mixture, and, as the calcium carbonate precipitates, it completely covers the available surface of the ash particles, which act as a substrate and provide nucleation sites 25 for precipitation and growth to occur. The core of mineral ash below the PCC surface has little or no effect on the optical and physical properties typically exhibited by a so-called "virgin" PCC, so that the "recycled" PCC produced can be used as a substitute for 30 virgin PCC in most processes or products where PCC is required with little or no adverse effect on product quality. Heat, water, and carbon dioxide produced by the combustion can be captured and recycled for use, as required, in the general process. In this manner, the waste of a typical deinking plant is substantially 35 reduced.

Description of the Drawing

Figure 1 is a flow chart of the process of

the present invention.

Detailed description of the Invention

A preferred embodiment of the invention is shown in Figure 1. Deink residue is heated in an oxygen-containing atmosphere to a temperature that is sufficiently high, typically 800° to 1200°C., so that all organic hydrocarbons are oxidized, and completely and efficiently incinerated. The primary products of this combustion are heat, carbon dioxide, water and mineral ash. If required, the mineral ash is first milled, and then an aqueous slurry is prepared by mixing the mineral ash with an aqueous slurry of calcium hydroxide ( $\text{Ca(OH)}_2$ ), which is formed by adding an excess of water to lime ( $\text{CaO}$ ). Calcium hydroxide slurry is also known as milk-of-lime, slaked lime or simply slake. A gaseous mixture containing carbon dioxide is bubbled through the slurry, where the calcium hydroxide and carbon dioxide react to form PCC. Reaction parameters such as temperature, gas concentration and addition rate, slake concentration, etc. are controlled in such manner to produce the desired PCC crystal size and morphology. In the current invention, the PCC has been found to precipitate and grow upon the surface of the mineral ash that is present in the slake. Advantageously, the combustion products from the heating process are recycled, with the water used to form the slurry, the carbon dioxide used to precipitate PCC, and the heat used to dry additional DIR prior to incineration. Upon completion of the reaction, the surface of the mineral ash has been coated with PCC to form composite particles with essentially the same optical and physical properties possessed by virgin PCC of similar size.

In another embodiment of the invention, mineral ash produced by the combustion of DIR is added to dry, unslaked lime ( $\text{CaO}$ ). An excess of water is

- 7 -

then added to the mixture to form a slurry of mineral ash and calcium hydroxide, and the carbonation reaction is then carried out as described above.

In a third embodiment of the invention, combustion of the residue is done as part of the calcination process in which limestone is converted to lime. This is possible because the temperature required for the calcination of limestone is similar to that required for efficient combustion of the DIR. Wet 10 DIR and limestone are combined and fed into a lime kiln with the relative amount of each adjusted so that the fractions of mineral ash and lime in the product of the calcination are correct for slaking and carbonation.

It also will be recognized that the heat and 15 carbon dioxide that are produced by the combustion of the hydrocarbon fraction of the DIR and are normally vented out the flue can be captured and recycled or redirected to earlier or later parts of the general process. Heat, for example, can be recycled back to 20 the kiln to aid in the drying of the residue that is required before combustion can occur. Carbon dioxide, generated as the hydrocarbon fraction of the residue is incinerated, can be captured and used to carbonate calcium hydroxide to PCC.

25 The fact that mineral ashes can be coated or plated with precipitated calcium carbonate is unexpected. In the current invention, this is possible because the mineral ash that results from the combustion of DIR is formed by a more complex chemical 30 reaction than simple calcination. For example, when kaolin clay ( $H_2Al_2Si_2O_8 \cdot H_2O$ ) or calcium carbonate is heated in a kiln to high temperatures, the calcined mineral phase is produced; i.e., calcined clay or calcium oxide. In the current invention, it has been 35 found that mixed mineral pigments react at high temperatures to form new, stable mineral phases. When calcium carbonate, kaolin clay and titanium dioxide are

- 8 -

mixed in various proportions and heated to 800° to 1200°C., typically 1000°C., two, three, or more new phases in varying proportion are produced, including Gehlenite ( $Ca_2AlSiO_7$ ) and/or Anorthite ( $CaAl_2Si_2O_8$ ) 5 with some Perovskite ( $CaTiO_3$ ). The relative amount of each phase formed will depend upon the amount of each mineral present in the original mixture and the combustion temperature. It is believed that these new 10 phases provide nucleation sites for the direct precipitation of calcium carbonate, which plates or is otherwise deposited onto the surface of the ash.

It can be readily seen that these mineral phases contain the same elements that make up the uncalcined mineral pigments, namely Calcium, Aluminum, 15 Silicon, and Oxygen. The high temperature of combustion is believed to cause these materials to react and rearrange to form thermodynamically stable mineral phases. The presence of calcium atoms in the crystal lattice of Gehlenite, Anorthite and Perovskite 20 renders the surfaces of these materials suitable as substrates upon which calcium carbonate can nucleate and grow. Calcium carbonate precipitates directly onto the surface of the ash particle, and completely covers or plates the particle with a layer of PCC that is 25 bound to the ash. The process of the present invention does not merely trap, cage, or entrain the ash by forming PCC particles that stick together to surround particles of the ash, but, instead, actually precipitates calcium carbonate directly onto the ash 30 surface to form a composite particle comprising an inner portion of mineral ash and an outer portion of PCC. The ash, in effect, acts as a "seed" and provides nucleation sites for calcium carbonate precipitation. Generally, the inner ash portion can comprise up to 35 about 50 percent of the weight of the particle. In a typical particle, the ash portion will be in the range of 5 to 30 percent, and preferably between 10 and 25

- 9 -

percent. Of course, the greatest amount of ash is desirable, so that the greatest amount of ash can be recycled. In this regard, a 50:50 ash:calcium carbonate particle is considered to be the optimum 5 formulation.

As deink residues are waste materials, the structure of the compositions will vary. Still, it also will be recognized that, if necessary, appropriate amounts of clay, titania, calcium carbonate or other 10 appropriate material can be added to the waste before incineration, to form the appropriate mineral phases during combustion.

There is reason to believe that the amounts of Gehlenite, Anorthite and Perovskite that can be 15 found in the recycled PCC of the current invention are lower than can be accounted for by collection and analysis of material losses throughout the process described herein. If losses are occurring that cannot be otherwise explained, then it is likely that some or 20 all of these mineral phases are being converted to PCC during the reaction. This may occur because of the relatively high pH in an aqueous slurry of calcium hydroxide, or because of other conditions that exist during the carbonation process.

The "recycled" PCC of the current invention, either alone or mixed with so-called virgin PCC, can be used in most applications where virgin PCC currently is used. PCC is commonly used in the production of printing and writing grades of paper that require 25 higher levels of functional mineral pigments, and recycled PCC can be used alone or in combination with virgin PCC in most of these applications. In a typical application, the amount of PCC would range from about 1 percent to about 50 percent of the mixture. Recycled 30 PCC can also be used where virgin PCC is now used in paint and filled polymer applications. As other 35 applications for virgin PCC are discovered, it is

- 10 -

likely that recycled PCC will also be found to be suitable. The examples indicate the qualities of the resulting recycled PCC, and one of ordinary skill in the art can easily determine the applications for which 5 recycled PCC is suitable. Combinations of recycled PCC and virgin PCC can be used, if desired or necessary, as both are compatible with regard to handling and processing as functional additives.

The surface area of the recycled and virgin 10 PCC particles was obtained using a Micromeritics Flowcarb 2300, which employs BET theory with nitrogen as the absorbing gas. The particle size was determined by a sedimentation technique, using a Micromeritics Sedigraph Model 5100 on an aqueous dispersion of the 15 product at about 3 percent, and using about 0.1 percent carboxylated polyelectrolyte (Daxad 30) as a dispersant. Dry brightness was measured using a Hunter LabScan.

Handsheets of a 60 g/m<sup>2</sup> paper were prepared 20 with a Formax Sheet former (Noble and Wood type, manufactured by Adirondack Machine Corporation) from a furnish of 75 percent bleached hardwood and 25 percent bleached softwood Kraft pulps beaten to 400 Canadian Standard Freeness (CSF) at pH 7 in distilled water.

25 Pulp consistency was 0.3125 percent. A synthetic sizing agent (alkyl ketene dimer) was added to the pulp at a level of 0.25 percent, equivalent to 5 lbs/ton of paper. Filler was added to the pulp furnish to achieve a target filler loading level. A retention aid (high 30 density cationic polyacrylamide) was added to the pulp at a level of 0.05 percent, equivalent to 1 lb/ton of paper. The sheets were conditioned at 50 percent relative humidity and 23°C. for a minimum of 24 hours prior to testing.

35 TAPPI brightness was measured using TAPPI test method T452-om92. TAPPI opacity was measured according to TAPPI test method T425-om91. Porosity was

- 11 -

measured on a Parker Print-Surf. Scott Bond was measured according to TAPPI test method UM-403.

Breaking length was measured according to TAPPI test method T494-om88.

5 Sizing was tested by the Hercules Size test (HST) to measure penetration of liquid through the handsheets. HST is the test method used to determine the degree of sizing of paper in the instant invention. The test was performed on a Hercules sizing tester  
10 Model KA or KC, and the test method employed was TAPPI Method T-530 PM-89.

EXAMPLES

15 The following non-limiting examples are merely illustrative of the preferred embodiments of the present invention, and are not to be construed as limiting the invention, the scope of which is defined by the appended claims.

20 Recycled PCC was produced from two samples of wet deink residue, received from a commercial deinking plant. The samples, as received, contained approximately 50 percent by weight water. The samples were dried in an oven at 100°C., and the composition of each sample of dry solids was analyzed with X-ray diffraction. The results of the analysis are given in  
25 Table 1. All values are given as percent by weight of dry solids.

TABLE 1

	I	II	
30	Organic Hydrocarbons	57-59	<50
	Calcite ( $\text{CaCO}_3$ )	11-12	30-40
	Kaolinite ( $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$ )	14-15	10-15
	Anatase ( $\text{TiO}_2$ )	2-4	2-4
	Amorphous Phases	<5	Not Detected
	Talc	0.5-1	0.5-1
35	Rutile ( $\text{TiO}_2$ )	0.5-1	0.5-1
	$\alpha$ -Quartz	0.5-1	Not Detected

- 12 -

EXAMPLE I

Residue Sample I was incinerated in a muffle furnace for 2 hours at 900°C. The ash recovered from the furnace was deagglomerated using a hammer mill, and 5 analyzed via X-Ray Diffraction (XRD). The results of the XRD analysis are given in Table 2. The values are approximate ranges given as percent by weight of total ash.

TABLE 2

10	Gehlenite ( $Ca_2Al_2SiO_7$ )	85-90
	Anorthite ( $CaAl_2Si_2O_8$ )	<5
	Perovskite ( $CaTiO_3$ )	5-10

To form a calcium hydroxide slurry, 1607.2 grams of water were added to 229.6 grams of CaO, while 15 vigorously stirring the mixture in a 4 liter stainless steel reactor equipped with a variable speed agitator. The calcium hydroxide slurry was passed over a 60-mesh screen before continuing the process. To the slurry were added 57.4 grams of the mineral ash of Table 2, 20 and the temperature of the slurry was adjusted to 35.2°C. A carbon dioxide containing gas (15 percent in air) was bubbled through this mixture with vigorous agitation until the reaction was complete at the end of 115 minutes at a pH of 8.0. The resulting product 25 was passed over a 325-mesh screen to remove grit, and the recovered +325-mesh residue was weighed and found to be only 10.661 grams. Scanning electron microscopy (SEM) and physical characterization of the recycled PCC were performed. The physical characteristics of the 30 dry recycled PCC product, prepared by plating the mineral ash of Table 2 with PCC, are shown in Table 3.

- 13 -

TABLE 3

Size Distribution via Sedigraph

5100:

5	90% smaller than	5.89 $\mu$ m
	50% smaller than	1.91
	20% smaller than	1.17
	10% smaller than	0.79
	BET Specific Surface Area:	8.7 $\text{m}^2/\text{g}$
10	Hunter Color Components (pigment):	
	L (Lightness)	95.9
	a	0.2
	b	1.8

Morphology via SEM: Scalenochedral

15 The recycled PCC produced in Example I was tested for its performance in paper in a handsheet study using a Kraft fiber furnish. The results of the handsheet study are given in Table 7, and show that the recycled PCC of the present invention can be used 20 effectively in papermaking in the same manner as virgin PCC.

Measurements of the TAPPI brightness of 25 handsheets incorporating recycled PCC and virgin PCC indicate that high paper brightness can be obtained with recycled PCC. The TAPPI brightness of handsheets incorporating recycled PCC from Example I is within about 2 percentage points of handsheets incorporating virgin PCC. Therefore, recycled PCC can be used without incorporating virgin PCC in applications where 30 maximum brightness is not required. The requirements of applications where maximum brightness is required or where control of the paper brightness is desired can be met by using a mixture of virgin PCC and recycled PCC. Preferred mixtures of virgin PCC and recycled PCC for 35 use in a high quality paper would be between 10 percent and 50 percent.

- 14 -

5 The difference between the TAPPI opacity of handsheets incorporating recycled PCC and those incorporating virgin PCC was about 1 percentage point, which is within the range of the statistical accuracy of these measurements. Therefore, the showthrough of paper incorporating the recycled PCC of the present invention is equivalent to papers incorporating virgin PCC.

10 The water resistance of handsheets incorporating recycled PCC, as measured in an HST test, was equivalent to that of papers incorporating virgin PCC as filler when comparing equivalent size fillers.

15 The strength of handsheets incorporating recycled PCC is essentially equivalent to or slightly better than handsheets incorporating virgin PCC.

However, the thickness of these handsheets is slightly greater than that of papers incorporating virgin PCC.

20 Finally, the porosity of recycled PCC papers is slightly higher than for virgin PCC, but not so high as to represent a significant disadvantage.

#### EXAMPLE II

25 Three (3) parts of deink residue Sample II (Table 1.) were combined with four (4) parts quarried limestone and placed in a pilot rotary kiln. The cylindrical kiln was gas fired, approximately 1.5 meters long and 16.5 cm in diameter. The kiln was set to operate at 1150°C., and nominal time of combustion was about 45 minutes. Following combustion, the lime/ash mixture was collected from the kiln and analyzed via XRD. The results are shown in Table 4. The results are given as the weight percent of the total of the total weight of limestone and deink residue.

- 15 -

TABLE 4

	Lime (CaO)	70-80
	Gehlenite (Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> )	10-15
	Anorthite (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )	7-10
5	Perovskite (CaTiO <sub>3</sub> )	1-2
	Microcline (KAlSi <sub>3</sub> O <sub>8</sub> )	1-2
	$\alpha$ -Quartz	0.5-1

To form a slurry of calcium hydroxide and mineral ash, 2009 grams of water were added to 287  
10 grams of the material of Table 4, while vigorously  
stirring the mixture in a 4 liter stainless steel  
reactor equipped with a variable speed agitator. The  
resulting calcium hydroxide/mineral ash slurry was  
passed over a 60-mesh screen before continuing the  
15 reaction, and 0.05 grams of residue were collected from  
the screen. The temperature of the slurry was adjusted  
to 35.5°C., and a carbon dioxide containing gas (15  
percent in air) was bubbled into the mixture under  
vigorous agitation until the reaction was complete at  
20 the end of 121 minutes when the pH of the slurry  
reached 8. The recycled PCC slurry was passed over a  
325-mesh screen to remove grit and other impurities,  
and 24.7 grams of +325-mesh residue were collected.  
Using XRD, the recycled PCC and the +325-mesh grit were  
25 analyzed, and the results are given in Table 5. The  
results are given as the weight percent of each  
material.

- 16 -

TABLE 5

		Recycled	+325-mesh
		PCC	Residue
	Calcite (CaCO <sub>3</sub> )	89-94	<0.5
5	Portlandite (Ca(OH) <sub>2</sub> )	<0.5	<0.5
	Gehlenite (Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> )	4-7	20-25
	Anorthite (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )	0.5-1	5-10
	Perovskite (CaTiO <sub>3</sub> )	1-2	20-25
	$\alpha$ -Quartz	0.5-1	20-25
10	Microcline (KAlSi <sub>3</sub> O <sub>8</sub> )	<0.5	20-25

The physical characteristics of the dry "recycled" PCC product of Table 5 are shown in Table 6.

TABLE 6

## Size Distribution via Sedigraph

15	5100:		
	90% smaller than		2.73 $\mu$ m
	50% smaller than		1.39
	20% smaller than		0.96
	10% smaller than		0.71
20	BET Specific Surface Area:		14.8 $m^2/g$
	Hunter Color Components		
	(pigment):		
	L (Lightness)		97.2
	a		0.0
25	b		1.1
	Morphology via SEM:		Scalenchedral

The recycled PCC produced in Example II was also tested for its performance in paper in a handsheet study using a Kraft fiber furnish. Again, the results 30 of the tests are given in Table 7, and show that the recycled PCC of the present invention can be used effectively in papermaking in the same manner as virgin PCC.

As in Example I, measurements of the TAPPI 35 brightness of handsheets incorporating recycled PCC and

- 17 -

5 virgin PCC indicate that high paper brightness can be obtained with recycled PCC. However, the TAPPI brightness of handsheets incorporating recycled PCC from Example II was equivalent, but at a slightly higher filler level, than that of handsheets incorporating virgin PCC.

10 Likewise, the TAPPI opacity of handsheets incorporating recycled PCC was equivalent to those incorporating virgin PCC, but at a slightly increased filler level. Therefore, the showthrough of the paper incorporating the recycled PCC of the present invention was essentially equivalent to that of papers incorporating virgin PCC.

15 The water resistance of handsheets incorporating recycled PCC, as measured in an HST test, was equivalent to that of papers incorporating virgin PCC as filler when comparing equivalent size fillers.

20 The strength of handsheets incorporating recycled PCC and virgin PCC was slightly lower than the control, again likely due to the differences in filler loading.

Finally, in Example II, the porosity of recycled PCC papers was slightly lower than that of virgin PCC paper, but well within an acceptable range.

- 18 -

TABLE 7

	PIGMENT	RECYCLED PCC EXAMPLE I	RECYCLED PCC EXAMPLE II	VIRGIN PCC 2.18 $\mu$ m	VIRGIN PCC 1.23 $\mu$ m
5	PERCENT FILLER	14.4	17.4	15.8	14.7
	OPACITY	87.5	88.6	86.8	88.6
	BRIGHTNESS	84.3	86.2	86.5	86.4
10	BREAKING LENGTH	2425	1946	2189	2242
	HERCULES SIZING	105	1	101	2
	SCOTT BOND	53	46	52	51
15	POROSITY	2203	1801	1958	2023

While it is apparent that the invention  
herein disclosed is well calculated to fulfill the  
objects above stated, it will be appreciated that  
numerous modifications and embodiments may be devised  
20 by those skilled in the art. It is intended that the  
 appended claims cover all such modifications and  
 embodiments as fall within the true spirit and scope of  
 the present invention.

- 19 -

C L A I M S

1. A composite particulate material comprising an inner portion of an ash of an inorganic mineral material, and an outer portion of calcium carbonate.
- 5 2. The composite particulate material of claim 1, wherein the calcium carbonate is precipitated onto the surface of the inner portion of inorganic mineral material.
- 10 3. The composite particulate material of claim 1, wherein said inorganic mineral material comprises an ash obtained from the incineration of wastepaper deink residue.
- 15 4. The composite particulate material of claim 1 or 2, wherein said inorganic mineral material comprises Gehlenite, Anorthite, Perovskite, or mixtures thereof.
5. A paper comprising cellulose fibers and the composite particulate material of claim 1, 2 or 3.
- 20 6. The paper of claim 5, further comprising virgin precipitated calcium carbonate, wherein the ratio of virgin precipitated calcium carbonate to composite particulate material is between about 99:1 and about 1:1.
- 25 7. A process for making precipitated calcium carbonate which comprises:
  - forming a slurry of calcium hydroxide and ash particles formed by incinerating a wastepaper deink residue at high temperature;
  - carbonating the slurry to precipitate calcium carbonate directly onto the ash particles; and
- 30 8. The process of claim 7, wherein the ash particles has been formed by incinerating wastepaper deink residue at a temperature of at least 800°C.
- 35 9. The process of claim 7, which further comprises adding at least one calcium, aluminum, or titanium compound or mixture thereof to the wastepaper

- 20 -

deink residue prior to incineration.

10. The process of claim 9, wherein the compound is calcium carbonate, titania, a clay, or mixture thereof.

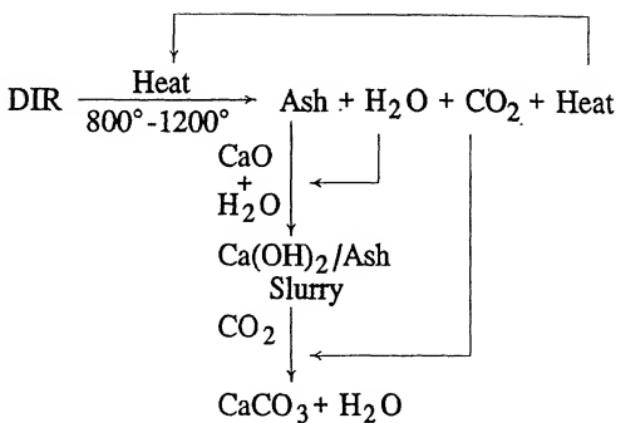
5 11. The process of claim 7, 8, 9 or 10, which further comprises forming a mixture of calcium hydroxide and water, and adding the ash to the mixture to form the slurry.

10 12. The process of claim 7, 8, 9 or 10, which further comprises mixing the ash with lime, and then adding water to the mixture of ash and lime to form the slurry.

15 13. The process of claim 7, 8, 9 or 10, which further comprises forming said slurry by mixing wastepaper deink residue with limestone, incinerating the wastepaper deink residue by calcining the mixture in a lime kiln to form ash and lime particles, and adding water to the particles to form the slurry.

20 14. A method of making paper comprising forming precipitated calcium particles according to the process of claim 7, 8, 9 or 10 and incorporating the particles in the paper as a functional additive.

15. The product produced according to the process of claim 7, 8, 9 or 10.



**Figure 1**

## INTERNATIONAL SEARCH REPORT

Inventor Application No  
PCT/US 96/03547A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09C3/06 C09C1/00 D21H17/67 D21H19/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09C D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 604 095 (ECC INTERNATIONAL) 29 June 1994 cited in the application see claims 1,9,12,14,15 ---	1,2,5,7, 14,15
A	DATABASE WPI Week 9014 Derwent Publications Ltd., London, GB; AN 90-102147 XP002005898 & JP,A,02 051 419 (KOMESHO SEKKAI KOGY , 21 February 1990 see abstract -----	1,2,7, 10,14

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another application or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered novel or to involve an inventive step when the document is considered in combination with one or more other documents, such combination being obvious to a person skilled in the art.

\*A\* document member of the same patent family

Date of the actual completion of the international search  17 June 1996	Date of mailing of the international search report  08-07- 1996
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl Fax: (+ 31-70) 340-3016	Authorized officer  Van Bellingen, I

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 96/03547

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-604095	29-06-94	AU-B- 8043094	22-06-95
		BR-A- 9404992	08-08-95
		CA-A- 2137951	15-06-95
		CZ-A- 9403152	12-07-95
		EP-A- 0658606	21-06-95
		FI-A- 945830	15-06-95
		JP-A- 8049186	20-02-96
		NO-A- 944783	15-06-95
		BR-A- 9305222	09-08-94
		FI-A- 935751	24-06-94
		GB-A- 2273701	29-06-94
		JP-A- 6226264	16-08-94